Polarographic Reduction of Azines in Acetonitrile

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The polarographic reduction potentials of some mono and diaza compounds were measured in acetonitrile solution and the reduction mechanism investigated by oscillopolarography and the Koutecky's analysis of the waves. Distinct regression lines were obtained for the two classes of compounds between the cathodic half-wave potentials and the energy of the lowest unoccupied Hückel π-molecular orbital.

The polarographic reduction potentials of some mono (1,2) and diaza compounds (3) have been recently measured in aprotic media, the purpose being to relate these potentials with the energy of the lowest unoccupied π-molecular orbital. The present measurements were undertaken in order to relate the Hückel molecular orbital energies with the reduction potentials of both classes of compounds measured under the same experimental conditions in an attempt to elucidate the mechanism of the electrode process by means of the oscillographic polarography and the calculation of the kinetic parameters $K_{f,h}$ (forward heterogeneous rate constant) and α (transfer coefficient).

The $K_{f,h}$ values were evaluated by the Koutecky's treatment of totally irreversible waves (4). $K_{f,h}$ and α are related by the equation $K_{f,h} = K^{\circ}_{f,h}\exp(-\alpha nFE/RT)$, where $K^{\circ}_{f,h}$ is the rate constant at E = 0 *vs* N.H.E.

For a wave due to a single rate-determining electrode process the plot of log $K_{f,h}$ *vs* E gives a straight line, but a curve is obtained if the electrode process involves two or more consecutive charge-transfer steps with similar kinetic parameters (5). For the azines good linear relationships have been obtained between log $K_{f,h}$ and E from which the values of $K^{\circ}_{f,h}$ and α n reported in the Table have been calculated.

The energy of the lowest unoccupied π-molecular orbital (K_{-1}, see Table) has been evaluated by the simple Hückel method, the following values being assumed for the parameters of the heteroatom: $h_N = 0.5$ and $K_{CN} = 1$. The coulomb integral for the nitrogen atom is given by $\alpha_N = \alpha_o + h_N \beta_o$ and the resonance integral of a bond between a nitrogen and a carbon atom is given by $\beta_{CN} = K_{CN} \beta_o$, where α_o and β_o are respectively the coulomb integral for the aromatic carbon and the resonance integral for an aromatic carbon-carbon π-bond.

Results and Discussion.

The experimental half-wave potentials ($E_{1/2}$) and the diffusion current constant (I_d) are reported in the Table.

A value of abour 4 for the I_d of an aromatic hydrocarbon in dimethylformamide is generally ascribed to a two-electron reduction. For quinoline an I_d value of 3.75 (6) and of about 4 (7) was reported. A higher value is to be expected in acetonitrile because of its lower viscosity (η = 0.344 m poise) than that of dimethylformamide (η = 0.802 m poise) (8). If the radius of the azines is assumed to be the same in both solvents the equation $I_d\, \eta^{1/2}$ = const. holds, this gives an I_d value of about 6 for a two-electron reduction process for a molecule of the size of quinoline in acetonitrile. The data in the table show that the compounds with two nitrogen atoms in the same ring (except the monocyclic diazines) give two distinct waves, the first being higher than the second, for an over-all two-electron addition. The monoaza compounds (except acridine and phenanthridine) give a single two-electron wave; in the *o*- *m*- and *p*-phenanthrolines, two two-electron waves are present. Isoquinoline and pyrimidine have abnormally low diffusion current constants. This feature was not investigated, but the effect of proton donors should probably be clarified (9). Benzo[c]cinnoline, benzoquinoxaline and phthalazine suffer further reduction at more negative potentials. Evidence for further reduction at a potential slightly above the background discharge is shown also by phenanthridine.

The slopes of the waves have been evaluated from the $E_{1/4} - E_{3/4}$ value (Table) which for a reversible one-electron addition equals 56 mV (10). Such a value rises to 84 mV for a reversible one-electron addition followed by a rapid chemical protonation reaction (11).

The results of the oscillographic polarography are reported in Fig. 1. For the compounds which give two one-electron cathodic peaks only the first has a corresponding, although less intense, anodic trace. In quinazoline it appears at a high scan rate. Phenazine is the only compound which shows two successive reversible electron additions. For most compounds a second anodic peak appears at a more positive potential but its intensity is greatly lowered if the anodic excursion starts from a potential less

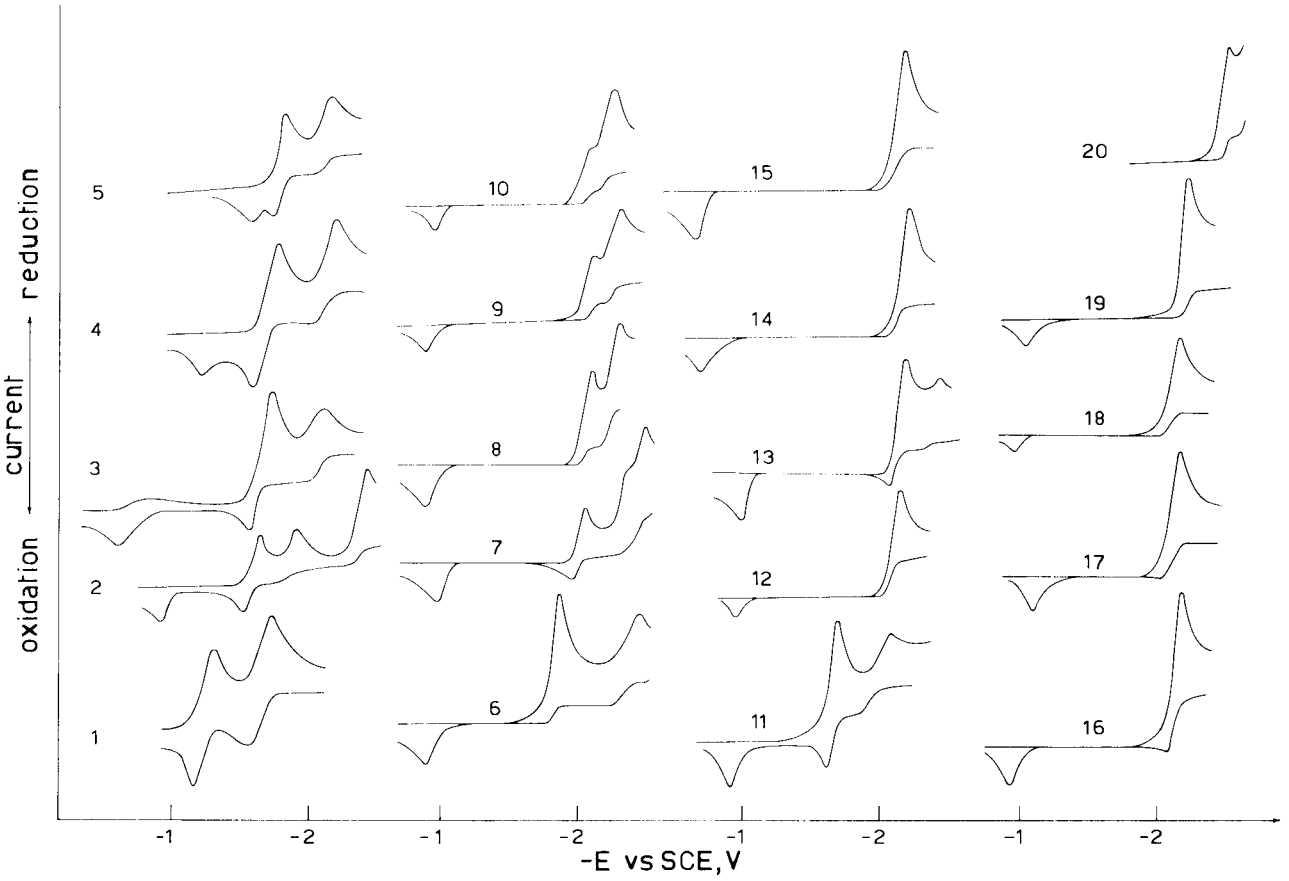

Figure 1. Oscillopolarograms of azines in acetonitrile 0.1 *M* tetraethylammonium perchlorate at 0.4 V/sec. The numbers refer to the compounds in the Table.

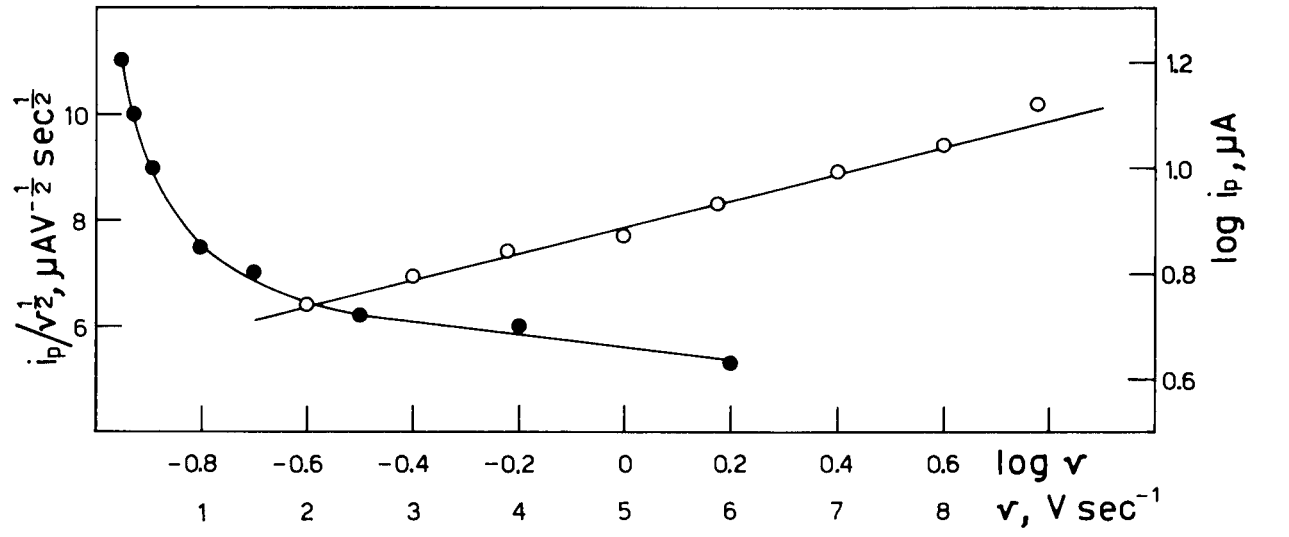

Figure 2. Dependence of peak cathodic current function $i_p/v^{1/2}$ on scan rate v (full points) and of log i_p on log v for the first peak of cinnoline in acetonitrile 0.1 *M* tetraethyl ammonium perchlorate.

negative than that of the second cathodic peak. It therefore results from the oxidation of an anionic species formed in the second reduction step and partially in the first step. This peak is also present in those compounds which show only a two-electron peak. No corresponding cathodic peak is observed during the next cathodic polarogram. Probably the oxidation product diffuses into the bulk of the solution during the time delay (about 5 seconds) between two successive polarograms. The current function $i_p/v^{1/2}$ (v = scan rate) is independent from v for the first cathodic peak of the phenazine but decreases with increasing v for all other compounds. Therefore, a fast irreversible chemical reaction follows the first reversible electron addition (12). The graph log i_p/log v is linear in any case with a slope between 0.3 and 0.4 μAV^{-1} sec. This behaviour is exemplified by the first peak of cinnoline, Fig. 2.

The experimental data suggest that the reduction of the azines follows a mechanism similar to that exhibited by the aromatic hydrocarbons (11,13) in aprotic media and represented by the scheme:

R	+	e	⇌	R^-		[1]
R^-	+	e	⇌	R^{--}		[2]
R^{--}	+	HS	→	RH^-	+ S^-	[3]
RH^-	+	HS	→	RH_2	+ S^-	[4]
R^-	+	HS	→	RH·	+ S^-	[5]
RH·	+	e	→	RH^-		[6]
RH^-	+	HS	→	RH_2	+ S^-	[7]

where HS is a proton donor, actually traces of water or the solvent itself (14).

For the compounds which show two one-electron waves the reactions [1] to [4] are assumed to occur; the dianion R^{--} is protonated in the reactions [3] and [4]. phenazine is the only compound which shows a stable doubly charged carbanion. If the radical anion RH^- is sufficiently stable during the potential sweep it can be revealed in the anodic polarogram. Its oxidation potential is expected to be more positive than the reduction potential of R since the electron affinity of RH is greater than that of the parent compound R (15). The most positive peak is therefore to be ascribed to the oxidation of RH^-. Moreover, it must be inferred in order to explain the greater height of the first wave as compared with that of the second, that R^- is partially protonated at the electrode to the radical RH·, which is promptly reduced at the same potential (equations [5] and [6]). RH^- is likewise produced also after the first electron addition.

The occurrence of a single two-electron wave for some compounds can be explained by the reactions [1] - [4] if the reaction [2] is faster than [1] or by the reactions [1] and [5] - [7], assuming that the rate of protonation of R^-

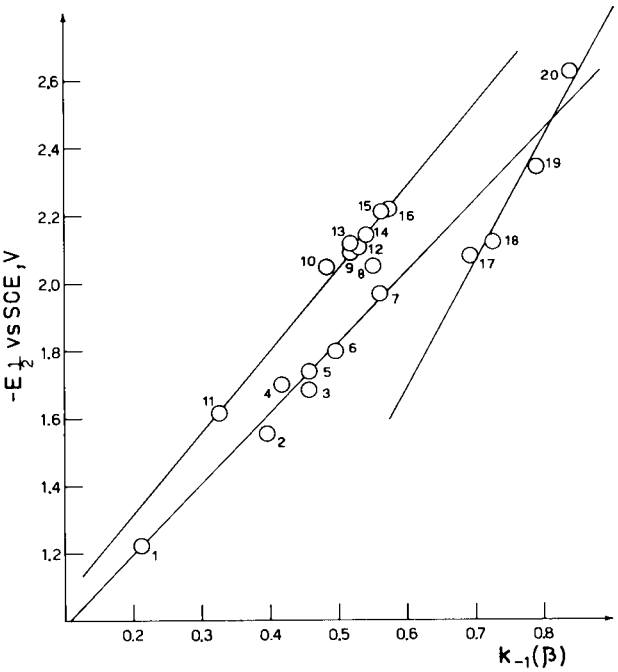

Figure 3. Dependence of half-wave reduction potential $E_{1/2}$ of azines on the energy of the lowest vacant π-molecular orbital K_{-1}.

is faster than the rate of diffusion of R^- away from the electrode surface. The first type of mechanism has been assumed for the one two-electron wave of styrene in acetonitrile and dimethylformamide (14), the second one in the reduction of nonaromatic conjugated hydrocarbons in dimethylformamide (16). We think that the latter mechanism is operating in the polarographic reduction of the azines by the following considerations: (a) the great sensibility of the polarographic characteristics of the azines to even small quantities of proton donors (3,7), as compared with the aromatic hydrocarbons; the charge localization on the heteroatom, as in the acridine monoanion compared with the anthracene monoanion (17) makes the azine radical anion R^- more basic than that of the corresponding hydrocarbon; (b) the values of $E_{1/4} - E_{3/4}$; (c) the current function data from the oscillopolarography; (d) the linear dependence of log $K_{f,h}$ on E.

The relation between $E_{1/2}$ and K_{-1} is shown in Fig. 3. It can be seen that the polycyclic monoaza and diaza compounds represent two well defined families; the regression lines are: monoaza compounds, $E_{1/2} = (2.422 \pm 0.057) K_{-1} - 0.842 \pm 0.029$; diaza compounds, $E_{1/2} = (2.090 \pm 0.105)K_{-1} - 0.780 \pm 0.046$ to be compared with the literature data:

monoaza compounds, $E_{1/2} = 2.127\ K_{-1} - 0.555$	$E_{1/2}$ vs Hg pool (1)
monoaza compounds, $E_{1/2} = 2.12\ K_{-1} - 0.484$	$E_{1/2}$ vs Hg pool (2)
diaza compounds, $E_{1/2} = 1.927\ K_{-1} - 0.813$	$E_{1/2}$ vs Ag/AgCl (3)

The *m*- and *p*-phenanthrolines (compounds with two nitrogen atoms in different rings) fit the regression line of the monoaza compounds; the *o*-phenanthroline does not.

A rough regression line can be drawn for the monocyclic derivatives $E_{1/2} = (3.702 \pm 0.345)\ K_{-1} + 0.519 \pm 0.262$.

TABLE I

Polarographic and Kinetic Data for the Reduction of Azines in Acetonitrile, 0.1 *M* in Tetraethylammonium Perchlorate, at 25° C. Concentrations between 0.5 and 0.7 m*M*.

Compound	$-E_{1/2}$ (a)	i_d (b)	$E_{1/4}-E_{3/4}$ (c)	$-\log K^{\circ}_{f,h}$ (d)	αn (e)	$-K_{-1}$ (f)
(1) Phenazine	1.227	3.04	62			0.208
	1.681	2.46	77	16.24	0.58	
(2) Benzo[*c*]cinnoline	1.554	3.34	68			0.394
	1.863	2.00	82	20.99	0.67	
	2.396	5.17	75	33.11	0.84	
(3) Cinnoline	1.686	4.70	62			0.454
	2.134	1.05	95	24.21	0.51	
(4) Quinoxaline	1.702	3.40	59			0.414
	2.163	2.32	98	20.45	0.55	
(5) Benzo[*f*]quinoxaline	1.744	3.28	65			0.455
	2.128	2.48	105	25.68	0.73	
	2.673	6.10	54	52.59	1.24	
(6) Quinazoline	1.799	3.07	57			0.495
	2.478	2.80	81	29.97	0.73	
(7) Phthalazine	1.976	3.98	58			0.559
	2.315	4.60	90	22.22	0.56	
	2.498	2.80	80	29.16	0.70	
(8) *o*-Phenanthroline	2.053	5.53	76	32.49	0.98	0.552
	2.269	5.32	84	27.78	0.74	
(9) *m*-Phenanthroline	2.092	4.88	70	35.74	1.06	0.519_8
	2.287	5.20	120	19.71	0.49	
(10) *p*-Phenanthroline	2.044	5.56	81	32.39	0.97	0.486
	2.229	5.42	74	28.96	0.78	
(11) Acridine	1.620	2.90	58			0.325
	1.994	2.55	88	19.41	0.57	
(12) Quinoline	2.105	5.60	73	33.08	0.97	0.527
(13) Phenanthridine	2.118	4.26	61			0.517
	2.415	1.25	82	21.72	0.52	
(14) Benzo[*f*]quinoline	2.140	5.55	63	40.90	1.20	0.535
(15) Benzo[*h*]quinoline	2.208	5.40	63	40.43	1.14	0.563
(16) Isoquinoline	2.220	4.04	70	33.74	0.94	0.576
(17) Pyrazine	2.080	6.30	73	30.56	0.90	0.686
(18) Pyridazine	2.120	6.35	75	28.54	0.83	0.727
(19) Pyrimidine	2.340	3.58	70	41.82	1.11	0.780
(20) Pyridine	2.622	6.33	82	37.14	0.87	0.841

(a) Half wave reduction potential in V *vs* S.C.E. calculated graphically from the plot $\log i/i_d - i$ *vs* E at $\log i/i_d - i = 0$. (b) Diffusion Current constant in $\mu AM^{-1}mg^{-2/3}sec^{1/2}$. (c) In mV. (d) Forward heterogeneous rate constant at E = O *vs* N.H.E., uncorrected for electrocapillarity. (e) Calculated from slopes of $\log K_{f,h}$ *vs* E plots. (f) Energy of the lowest vacant molecular orbital in units of β_o.

The occurrence of these distinct correlation lines suggests that the solvation energy is different for the different families of compounds while with a family it can be considered constant or varying according to the electron affinity of each compound. Probably a different charge distribution on individual atoms in the molecule is responsible for this behaviour. The solvation energy in the present compounds does not depend only upon the radius of the molecule as predicted by the simple Born equation (18) - $\triangle G_{solv} = Ne^2 (1-1/D)/2r$.

EXPERIMENTAL

Chemicals.

m-Phenanthroline, m.p. 78°; *p*-phenanthroline, m.p. 173°; quinazoline, m.p. 48-49° and benzo[*f*]quinoline, m.p. 62°, were prepared and purified according to literature methods. All other compounds were commercial substances and were purified by crystallization or distillation. Tetraethylammonium perchlorate (Erba polarographic reagent) was used without further purification. Acetonitrile (Erba, R.P.) was purified by drying over phosphorus pentoxide followed by distillation.

Apparatus.

Polarograms were recorded with a Leeds and Northrup Electro-Chemograph type E and single sweep oscillopolarograms with an Amel oscillopolarograph Model 448. A water-jacketed two-compartment cell maintained at 25±0.5° was used in all experiments. In one arm of the cell was inserted, by means of a saturated potassium chloride agar bridge, a large surface aqueous S.C.E. The supporting electrolyte, 0.1 *M* tetraethylammonium perchlorate, had a discharge potential of about - 2.8 V *vs* S.C.E. The overall cell resistence including solution, bridge and reference electrode, was about 3500 ohms at the end of the drop life. The test solutions were deoxygenated with electrolytically generated hydrogen for 10 minutes. The dropping mercury electrode had the following characteristics in the test solution at a mercury height of 50 cm. and on open circuit: m = 0.70 mg/sec and t = 6.5 sec/drop, giving $m^{2/3}t^{1/6} = 1.077$. The potentials, corrected for IR drop, are referred to the S.C.E. and include liquid junction potentials.

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